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Determination of Parts-per-Billion Vinyl Chloride Monomer in Vinyl Chloride Copolymers by Use of an Automated Headspace Analyzer with an Electrolytic Conductivity Detector*

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Abstract

A headspace, gas chromatographic method, which is suitable for the routine determination of low-level vinyl chloride monomer (VCM) in a variety of vinyl chloride (VC) copolymers, has been developed. This method utilizes a Perkin-Elmer F-45 headspace analyzer modified to accommodate a Tracor model 700 Hall electrolytic conductivity detector (HECD). The HECD provides the selectivity necessary to resolve interferences that are prevalent in this type of system and the sensitivity needed for parts-per-billion (ppb) determination. With a linear response over the range of 12 × 10^{-9} g to 2 × 10^{-6} g of monomer, this system provides a practical lower limit of quantitation of 3 ppb based on polymer weight. Using this method the ability to analyze a variety of VC copolymers in various physical forms is demonstrated.

Introduction

In recent years numerous procedures for determination of VCM at the ppb level have been described in the literature (1–3); however, most of them are not suitable for the analysis of substantial numbers of samples, since they depend on sophisticated instrumentation requiring highly-trained operators and involve lengthy analysis times. The objective of this present effort was to develop a simple, rapid, and reliable procedure that can be used to determine ppb levels of VCM in a variety of different VC copolymers.

The comonomers utilized in current commercial vinyl copolymers include vinyl acetate (VAC), maleic anhydride, and vinylidene chloride. Polymerization techniques and processing methods used by the major manufacturers differ substantially, which results in the possibility that a wide variety of volatile components may be present in the final product. Therefore, a method must permit resolution of low-level VCM from a very heterogenous matrix in order to be generally useful. In addition, these copolymers must be handled in a variety of forms including solids, such as powders, pellets, films, or plaques, and liquids, such as solutions and emulsions.

One of the most generally useful methods for the analysis of VC copolymers on a nonroutine basis was developed by Dennison and Breder (1). It involves sparging a dimethylacetamide (DMAC) solution of the polymer, trapping the volatiles in a cold ethanol solution, chromatographing an aliquot of the ethanol headspace on a porous polymer column, and quantitating with a flame ionization detector (FID). This method will readily quantitate VCM down to the 1-ppb level. Unfortunately, it is far from being simple and rapid; the equipment is complex, some of the manipulations are hazardous, and a skilled operator is needed to ensure accurate measurements.

Direct headspace is an effective method of separating volatile components from polymeric samples, since it avoids overloading the analytical system with solvents and other high-boiling components. Automation of the process not only improves analytical precision, but also increases productivity. Because a large number of organic impurities are found in the copolymers and solvents used, the problem of resolving low-level VCM from this matrix can be greatly simplified by the use of a halogen-specific detector. For many chlorine-containing compounds, electron capture is the detector of choice because it provides high sensitivity along with specificity. Unfortunately, VCM does not show any more response with an ECD than it does with an FID (1). Two approaches that increase the response of an ECD to VCM—bromination of the VCM (2) and use of doped make-up gas (3)—are not applicable to routine analyses. Therefore, the most practical detector for the quantitation of ppb levels of VCM in this type of system is the HECD operated in the reductive mode.

Experimental

The automatic headspace analyzer used was a Perkin-Elmer F-45 equipped with an FID and a backflush accessory. This

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analyzer was modified to accept a Tracor model 700 HECD. After removal of the sheet metal skin on the left side of the analyzer's column oven, the HECD furnace bracket was fastened to the oven frame by self-tapping screws. The bracket was positioned so that the furnace assembly would be aligned with an existing hole through the column oven wall. As illustrated in Figure 1, the unit containing the circulating pump, electronics, and power supply for the HECD was positioned to the left of the F-45 carousel. The transfer line to the HECD furnace was passed through the existing hole in the oven wall and coupled directly to the chromatographic column with an adapter, as indicated in Figure 2. This adapter was mounted on the bracket intended for mounting the "A" FID detector. With this arrangement, columns in the standard F-45 configuration can be used.

Headspace analyzer parameters (see Table I) were optimized for a range of VC-VAC copolymers, either as solid resins or as solutions. DMAC is an excellent solvent for VC copolymers: it has a high boiling point and is readily available in a high state f purity. The chromatographic parameters were chosen to give the lowest practical limit of quantitation; when higher levels (greater than 100 ppb) of VCM are present, shorter turnaround times can be achieved by reducing backflush and equilibration times.

Samples to be analyzed should be handled with care, as should be done in any trace analysis. Finely divided powders and thin films will lose VCM rapidly if exposed to the atmosphere. Therefore, this type of sample should be transported in a sealed container with a minimum amount of free space. These samples should be analyzed in as short a time as possible and refrigerated, if storage is necessary. Grinding of samples to reduce particle size may lead to loss of monomer and should be avoided.

Sample preparation involves dispersing 4 g of polymer in sufficient DMAC to give a total volume of 14 ml. Dissolution of high-molecular-weight polymers and copolymers may require shaking for periods of up to 18 hr to give homogenous solutions, particularly when the polymer is in the form of thick sections. Products that are finely divided or in the form of fine powders will dissolve rapidly if mixing is started as soon as the solvent comes in contact with the solid polymer.

It is essential in calibrating headspace methods that the calibration standards be as close to the composition of the actual sample as possible. This is particularly important in cases when the sample being analyzed contains appreciable quantities of volatile species such as water or organic solvents, since they can substantially change the recovery of monomer. The preferred method of calibration is by standard addition; in this procedure, measured quantities of VCM are added to a DMAC solution of the polymer system being investigated. The most convenient form of low-level VCM standard is a commercially prepared (e.g., one from MG Scientific Gases) mixture of the monomer in an inert gas. These standards are stable and generally can be stored under ambient conditions for six months or more. Caution must be exercised in introducing the measured amount of gas standard into the sample vial by syringe, since use of an oversized or deformed needle can cause the septum to leak under pressure.

Results and Discussion

Examination of typical VC-VAC copolymers showed that the selectivity obtained by using the separating power of the headspace sampling technique and the halogen specificity f the detector gives complete resolution of the VCM peak (see Figure 3). This is in marked contrast to the complex, poorly resolved chromatograms obtained when attempts were made to determine ppb-level VCM in this type of coppolymer using a flame detector and direct injection of polymer solutions. Direct calibration of the detector with VCM over the range of 0.13 to 26 ng (Figure 4) gave a linear plot.

In order to determine accuracy, a set of six samples was analyzed by this method and by the "FDA Method" (1), which is considered to be the most reliable general method currently

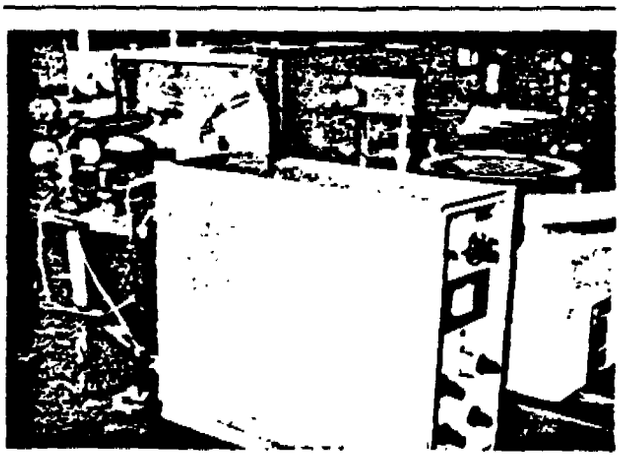

Figure 1. Overall view of F-45/HECD assembly

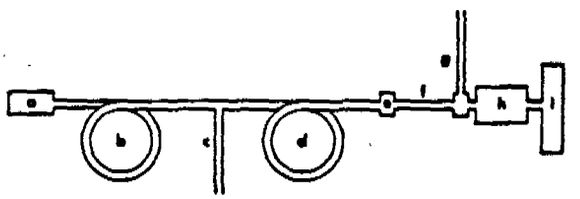

Figure 2. F-45/HECD Plumbing: Components: a. injection assembly; b. 3-ft column; c. backflush gas inlet; d. 6-ft column; e. adapter fitting; f. glass-lined transfer line; g. aux. H_2; h. HECD pyrolysis furnace; i. HECD conductivity cell

Table I. Analytical Parameters

Column	2.7-m × 3.2-mm o.d.; stainless steel packed with 60/80 mesh Tenax GC (tee fitting inserted 0.9 m from injection end of column to provide for backflushing)
Carrier Gas	Nitrogen at 1.2 bars (27 cc/min)
HECD Flows (cc/min)	H_2-28; electrolyte, 0.5
HECD Electrolyte	Isopropanol:water (1:1)
Temperatures (°C)	Carousel, 80; needle, 100; column, 70; HECD furnace, 880
Times (min)	Preheat, 60; inject, 0.15; run, 9; backflush 40.
Sample	4 g of polymer with DMAC added to give 14 ml of total volume

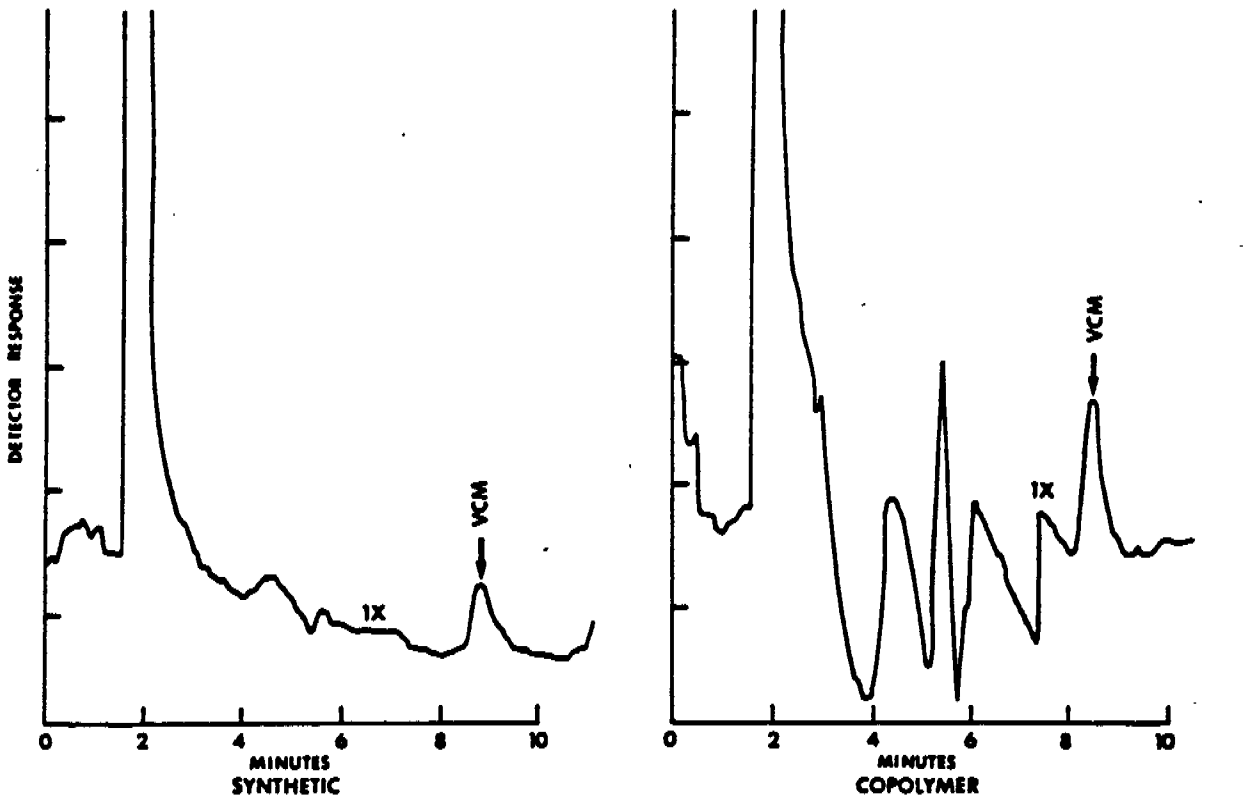

Figure 3. Chromatogram from the headspace from a synthetic of 13 × 10⁻⁹ g VCM in 14 ml of DMAC and from 14 ml of DMAC solution containing copolymer

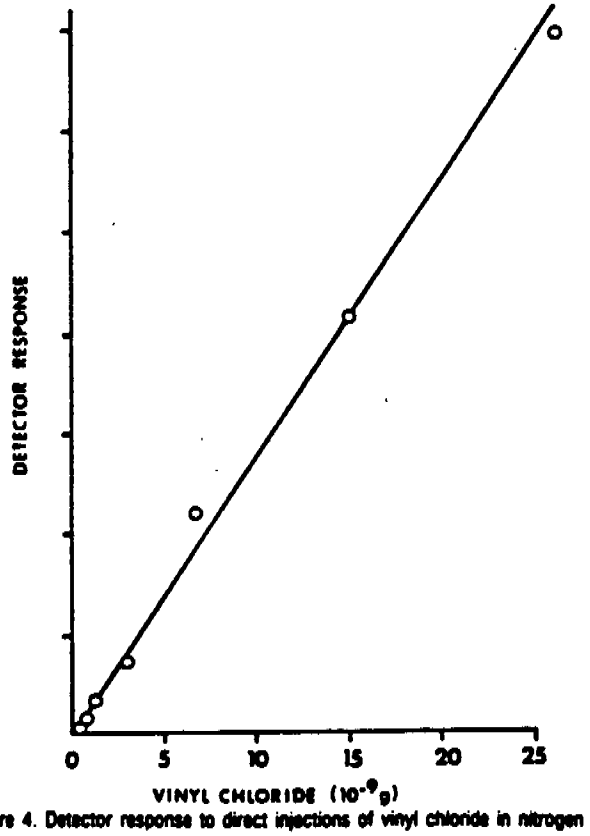

Figure 4. Detector response to direct injections of vinyl chloride in nitrogen

Table II. Comparison of Current Procedure with FDA Method (ppb)

	This Method (HECD)	FDA Method* (FID)
VC Copolymer A	4	110
VC Copolymer B	6	8
VC Copolymer Solution	5	420
VC Homopolymer A	7	5.5
VC Homopolymer B	14, 14, 13	13
Saran™	33	12 13

*See Reference 1.

available. As shown in Table II, the agreement is excellent for the copolymer B sample and the two homopolymers. The high results obtained in the case of the other two copolymer samples are due to interfering organics; in the case of copolymer A, this was shown by mass spectrometry to be a 4-carbon hydrocarbon. A limited amount of sample prevented determinati n of the cause of the poor agreement in the case of Saran™; it might have been due to a random error. The estimated precision of the method in terms of standard deviation is 20% at 6 ppb and 2.1% at 810 ppb.

In surveying different types of VC copolymers, this method was found to be generally applicable for determining VCM down to 3 ppb. The most important caveat is that the system must be recalibrated, gener-lly by the standard addition method, whenever a new type of copolymer is examined. This is particularly important with systems containing solvents differing in polarity or other comonomers that may change copolymer

characteristics. For example, when a typical VC-VAC-vinyl alcohol terpolymer is dissolved in DMAC to give a 29% solution, the concentration of substituent groups as mole fractions would be 0.64 amide, 0.32 chloride, 0.011 acetate, and 0.030 alcohol. Obviously the acetate and/or alcohol could be doubled, halved, or eliminated altogether without changing the concentration of the major components significantly. On the other hand, replacement of a substantial fraction of the amide solvent by one of different polarity, such as an aromatic hydrocarbon or water, would have a substantial effect on the partition coefficient and would therefore require a new calibration.

Conclusion

The Perkin-Elmer F-45 headspace analyzer can be modified readily to accept the Tracor model 700 electrolytic conductivity detector. This system can be used, on a routine basis, to determine vinyl chloride monomer down to 3 ppb in a variety of vinyl chloride copolymers and in homopolymer. Comparison of results obtained by this method with data from a proven sparge and trap method shows a high degree of agreement.

References

1. J.L. Dennison, C.V. Breder, T. McNeal, R.C. Snyder, J.O. Reach, J.A. Sphon. *JAOAC* **61**: 6813 (1978).
2. P.D. Golden, F.C. Fehsenfeld, W.C. Custer, M.P. Phillips, R.E. Sievers. *Anal. Chem.* **52**: 1751 (1980).
3. D.T. Williams. *JAOAC* **59**: 32 (1976).

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